Noblest of All Metals Is Structurally Unstable at High Pressure

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In a series of experiments in externally electrically heated diamond anvil cells we demonstrate that at pressures above ~240 GPa gold adopts a hexagonal–close-packed structure. *Ab initio* calculations predict that at pressures about 250 GPa different stacking sequences of close-packed atomic layers in gold become virtually degenerate in energy, strongly supporting the experimental observations.

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The uniqueness of gold and its special role in human society throughout the whole history is closely related to its exceptional stability to chemical reactions and extreme pressures and temperatures [1–4]. The stability of the solid phase of gold in its face-centered cubic (fcc) structure at pressures up to at least 180 GPa has been earlier shown experimentally [5–8]. Gold has been in focus of high-pressure research for several decades as a primary equation of state (EOS) standard [4,8]. Advances in high-pressure techniques require standards which are applicable at multi-megabar pressure range. Large pressure and temperature stability ranges of the fcc phase and its large isothermal compressibility make gold a very attractive material to be used as a pressure marker above 100 GPa [8–10]. Possible pressure-induced phase transition in gold will place a "natural" limit on the application of fcc-Au as a standard. Laser-driven shock waves experiments [4] did not detect any transitions along the Hugoniot curve up to 10 TPa. Theoretical calculations, however, predict a fcc-to-hcp-phase transformation at pressures between 2 and 4.1 Mbar [10,11] (difference in the transition pressure depends on methods and details of calculations). There is also a theoretical possibility [10] of structural phase transformations to complex structures [12,13] triggered by electronic $s \rightarrow p$ or $s \rightarrow d$ transitions.

We studied the behavior of gold experimentally at pressures above 270 GPa and temperatures between ambient and 1100 K in externally electrically heated diamond anvil cells [14,15]. The details of the experimental procedures are described in our earlier papers [14–16]. In externally electrically heated diamond anvil cell (DAC) temperature gradients within the pressure chamber are practically absent and accuracy in temperature measurements with a thermocouple is within 20 K. *In situ* high-P, T experiments were conducted in externally electrically heated DACs. Laser heating was used for relaxing stresses, and x-ray patterns were taken from temperature-quenched samples at high pressure. Attempts to conduct laser-heating experiments at pressures above 180 GPa failed due to high reflectivity of the gold and/or small thickness of the sample. (We found also that the fcc gold phase is temperature quenchable (see below) which limited the application of the laser-heating technique).

Diamonds with culet sizes of 250 to 60 μm have been used. In experiments above 100 GPa we employed beveled diamonds with central culets of 150 μm, and above 150 GPa double beveled diamonds with culets of 60 μm were used. As gasket material Re or Ir were employed. For experiments aiming to reach pressures above 100 GPa the initial holes of 40 to 45 μm in diameter were made (the thickness of indentation and the diameter of the pressure chamber were optimized in such a way that at pressures above ~80 GPa a sample of gold covered completely the smallest facet of the beveled diamond). In experiments below 100 GPa diamonds were mounted on the seats made of B_4C or cBN with 70° total opening angle, while at pressures above 100 GPa we employed seats made of hard metal (cobalt doped WC or Nemonic) with slits with maximum opening of 45°. We conducted *in situ* x-ray high-pressure experiments in the Bayerisches Geoinstitut (Germany) and at ESRF (France). At ESRF powder diffraction experiments were conducted at the beam lines BM01, ID30 and ID27. At the BM01 beam line the data were collected with the MAR345 detector using an x-ray beam of 0.6996 Å wavelength and a size of 50 × 50 μm. At ID30 and ID27 we used MAR345 or Bruker CCD area detectors and a highly focused beam (8 × 10 μm). In Bayerisches Geoinstitut we obtained powder x-ray diffraction data with a system consisting of Rigaku FRD high-brilliance generator (90 kW) and APEX CCD Area

Detector. The MoK_α radiation (tube voltage 60 kV, tube current 55 mA, cathode gun 0.1 × 0.1 mm) was focused with MaxFlux x-ray optics and further collimated down to ∅30 μm FWHM beam size. All experiments at pressures above 150 GPa were conducted in the Bayerisches Geoinstitut and, to the best of our knowledge, it is the first report of application of in-house x-ray facilities at a multimegabar pressure range. The collected images were integrated using the FIT2D or GADDS programs in order to obtain a conventional diffraction spectrum.

Pressure characterization above 150 GPa, especially at high temperature, is a challenging task. Most of our earlier experiments at pressures below 150 GPa were not especially made to study gold or its equation of state. Instead, we used gold together with other materials (Cu, Pt, and at pressures below 30 GPa NaCl) as internal standards in experiments designed to investigate the behavior of various oxides and silicates at elevated pressures and temperatures. Those experiments, however, opened for us a possibility of using the EOSs of NaCl [17], Cu [8], or Pt [8,18] to check how the existing equation of state of Au describes the P-V-T behavior of gold. Figure 1 shows variation of the unit cell volume of gold at ambient temperature and at temperatures 1020 to 1070 K (data were collected in six different experiments; all data points at intermediate temperatures were omitted for clarity). In agreement with previous studies [8–10], we found that at pressures up to at least 150 GPa and temperature ~1050 K Anderson's *et al.* [19] thermal equation of state (TEOS) describes our data within the error bars of the measurements of pressure, temperature, and volume. (Note that although accurate characterization of pressure in our experiments is important, any possible systematic errors in the pressure scale cannot affect major conclusions of our study related to phase stability of gold). In experiments above 150 GPa and high temperatures in order to avoid any possible chemical reactions or metals alloying, we loaded only gold (99.9999% purity; Goodfellow, Inc.) into the pressure chamber and relied on the fcc-Au TEOS as an internal pressure standard.

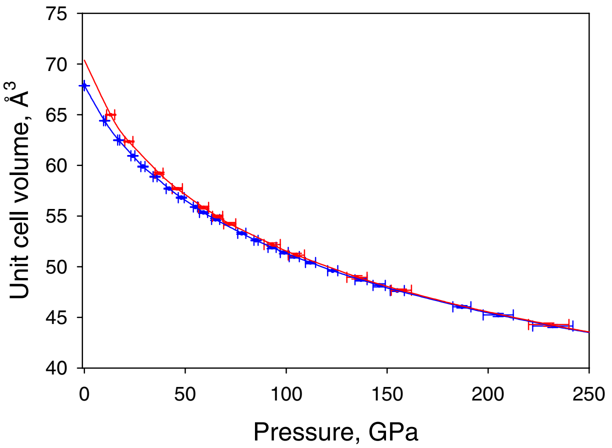

FIG. 1 (color online). Variation of unit cell volume of fcc-Au at ambient temperature (blue or dark gray symbols) and at temperatures 1020 K to 1070 K (red or light gray symbols) (data collected in six different experiments; all data points at intermediate temperatures omitted for clarity). In agreement with previous studies [8–10] we found that at pressures up to at least 150 GPa and temperatures up to 1050 K Anderson *et al.* [19] thermal equation of state (TEOS) (solid lines—lower one for 300 K, upper one for 1050 K) describes our data within the error-bars of the measurements of pressure, temperature, and volume. In the experiments above 150 GPa and high temperatures, in order to avoid any possible chemical reactions, we loaded only gold (99.9999% purity; Goodfellow, Inc.) in the pressure chamber and relied on fcc-Au TEOS as the internal pressure standard.

We conducted three experiments at pressures above 150 GPa and high temperature on pure gold (Figs. 2 and 3). Upon heating up to 1070 K at pressures below ~230 GPa we observed only fcc-Au (Fig. 3). On compression at room temperature fcc-Au phase preserved at least to 275(20) GPa [Fig. 2(a)]. On heating the pressure decreased to 248(20) GPa at 860(10) K and we detected the appear-

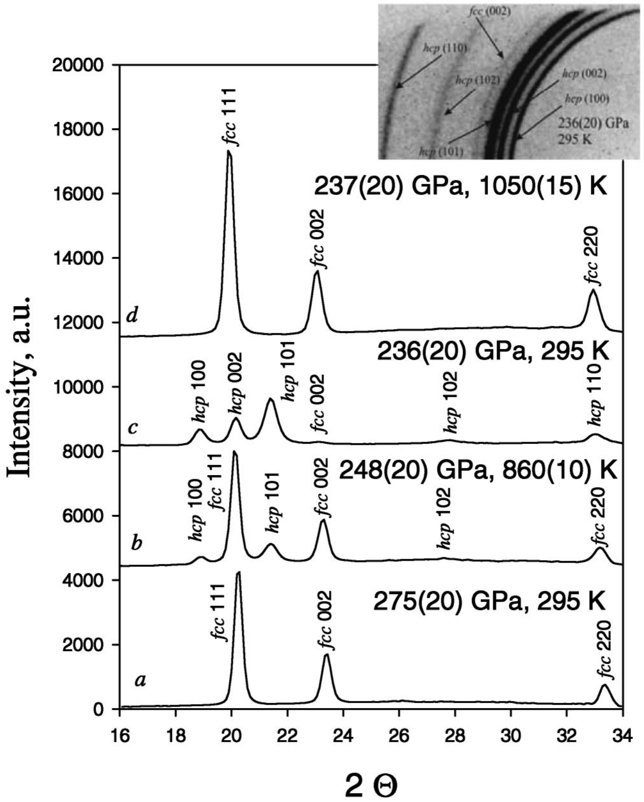

FIG. 2. Examples of diffraction pattern collected from gold (a) compressed at ambient temperature to 275(20) GPa, (b) heated at 860(10) K at 248(20) GPa, (c) slowly cooled down to room temperature at 236(20) GPa, and (d) heated again to 1050(15) K at 237(20) GPa. The inset shows part of 2D diffraction image of the sample at 236(20) GPa and room temperature. The pattern is dominated by diffraction lines of the high-pressure hcp-Au phase.

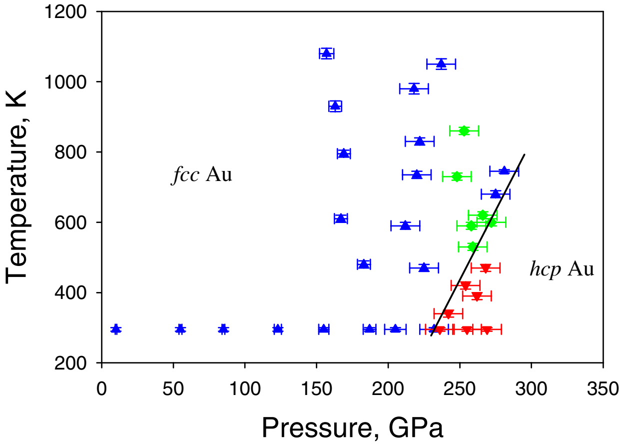

FIG. 3 (color online). Phase relations between fcc (blue triangles) and hcp (inverse red triangles; amount of hcp-Au above 80%) gold phases as was observed in three independent multimegabar pressure experiments. Green diamonds show conditions of phase coexistence (fcc-Au above 20%). The solid line indicates the tentative phase boundary between the fcc- and hcp-Au phases.

ance of new diffraction lines [Fig. 2(b) and Fig. S1 in Ref. [20]] which could be easily indexed in a framework of the hcp structure with lattice parameters $a = 2.490(2)$ Å and $c = 4.060(10)$ Å, $V = 6.56(2)\ \mathrm{cm^3/mol}$ [the coexisting fcc phase has the lattice parameter $a = 3.520(1)$ Å and $V = 6.57(1)\ \mathrm{cm^3/mol}$]. When the sample was slowly cooled (over about 8 h), we observed a gradual increase of the amount of hcp phase, and at room temperature and 236(20) GPa the content of the remaining fcc phase fell by about 10% [Fig. 2(c) [20]; the fcc phase has the lattice parameter $a = 3.531(3)$ Å and $V = 6.63(1)\ \mathrm{cm^3/mol}$; hcp phase has the lattice parameters $a = 2.504(1)$ Å and $c = 4.053(3)$ Å, $V = 6.62(1)\ \mathrm{cm^3/mol}$]. When synthesized, at ambient temperature the hcp phase could be compressed to 270 GPa (on an attempt of further pressure increase the diamonds failed), and on decompression at ~230 GPa it transforms back to the fcc phase (Fig. 3). Heating of hcp-phase-predominate samples at pressures above ~230 GPa results in transformation to fcc phase [Figs. 2(d) and 3]. Further compression at high temperature (600–800 K) of the materials containing both hcp and fcc phases results in complete transformation into the fcc phase (Fig. 3). In one of our experiments, due to failure of the heating element, temperature decreased very quickly (from ~1000 to ~450 K for 10–15 s) and as a result the fcc phase quenched even at 245 GPa. Investigation of the samples quenched to ambient conditions using scanning electron microscopy and microprobe with the resolution down to submicrometers, as well as unchanged before and after experiments lattice parameters of Au justified the absence of chemical reaction(s) in the samples. In summary (Fig. 3), our data indicate that fcc-Au transforms to hcp-Au and that the transition pressure increases with increasing temperature.

Changes of the molar volume across the fcc-to-hcp-phase transition are small (practically within the precision of measurement, although there are indications that the hcp phase is slightly denser). A small volume effect on the transition could explain a wide range of the coexistence of the phases (see, for example, Ref. [19]) and suggests that it would be very difficult to detect such a transition in shock wave experiments [4]. Further studies are required in order to elaborate the effect of the phase transition in gold on its TEOS, although small volume changes advocate that the compressibility and thermal expansion of hcp- and fcc-Au at corresponding pressures and temperatures are very close.

We first notice the well-known fact that the fcc and hcp structures differ only by the stacking sequence of close-packed layers, *ABCABC* and *ABAB*, respectively. In Fig. 4 the calculated enthalpies of different stacking arrangements of the close-packed layers in Au as functions of pressure are shown (see Ref. [20] for computational details). The presented stacking configurations contain three main close-packed fragments of the fcc (*ABC*), hcp (*ABAB*), and double hexagonal close-packed (dhcp) (*ABAC*), as well as a number of their combinations. The

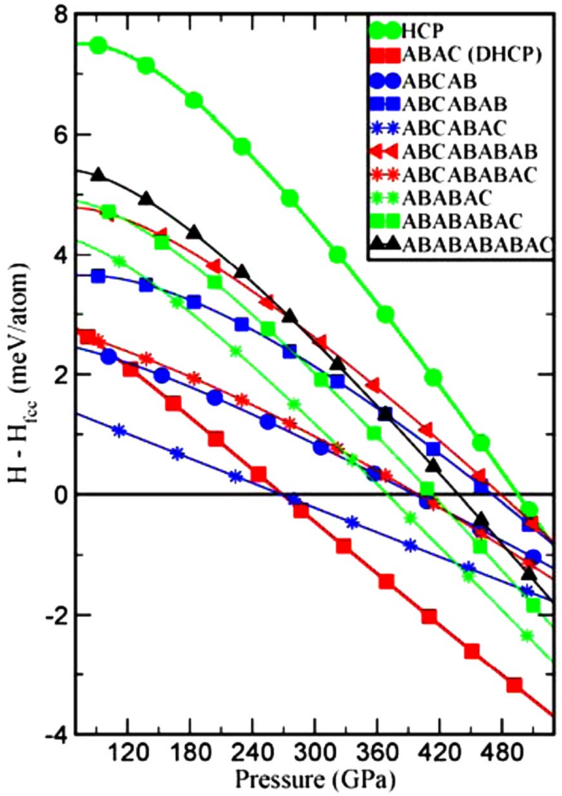

FIG. 4 (color online). Calculated enthalpies of different arrangements of the close-packed atomic layers in gold under compression. The enthalpy of the fcc phase is taken as reference and is shown by a horizontal full line.

most remarkable feature is that at pressures of interest, i.e., above 200 GPa, the enthalpy difference among different close-packed stacking arrangements in Au is just about 5 meV (~75 K). Nevertheless, the ground-state fcc structure of Au remains most stable up to about 260 GPa. At higher pressures the enthalpy differences of different stacking configurations with respect to the fcc structure become negative, indicating an instability with respect to the stacking fault formation and eventually a phase transformation. According to our calculations the *ABAC* (dhcp) stacking becomes the most stable at high pressures. However, the enthalpy differences among all considered stacking arrangements are extremely small, not exceeding a couple of meV (less than 20 K), which is at the border of the accuracies of best to date *ab initio* methods. Although in our experiments we did not see clear evidence of superlattice reflections [for example, (103) reflex of the dhcp phase] we observed coexistence of the fcc and hcp phases over a wide pressure and temperature range, which suggests that these two phases are energetically very close to each other. We also notice that it has been shown [21,22] that cold working, if applied to a metal at the preparation stage, may favor small shear distortions promoting the change in the phase sequence under pressure.

Recently fcc-hcp transition was found in Al at 217(10) GPa by compression at room temperature. Remarkably, the close chemical and structural elemental analogues of gold, for example, Cu, Ag, Pt, are not expected to undergo phase transformations at least in a 300 GPa pressure range [14]. Our theoretical results (see Ref. [20]) show that these elements remain stable in the fcc structure up to at least 500 GPa. In the case of Pt, the difference in high-pressure behavior stems from the fact that the d shell of Pt is not completely filled compared to the d shell of Au. According to the canonical d-band model [23,24] this stabilizes the fcc vs the hcp phase. In the case of lighter elements isoelectronic to gold, the $d \rightarrow sp$ electron transfer, in particular, favoring the fcc-to-hcp transition [25] is considerably lower in Cu and Ag compared with Au (see Fig. S3 in Ref. [20]), preventing a phase transition at least up to 500 GPa. The differences in the $d \rightarrow sp$ electron transfer are due to less pronounced relativistic effects in the lighter elements Cu and Ag. To conclude, our work suggests that although gold is in many respects the noblest of all elements, structurally it is in fact "less noble" than copper, silver, and platinum.

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